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Surface and hardness studies on as-grown {100} faces of zinc (tris) thiourea sulphate crystals

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Abstract : Single crystals of zinc (tris) thiourea sulphate are grown at 30°C by slow evaporation method. Surface studies have been carried out on a number of {100} faces of these crystals. Typical striations are observed on these faces, mostly they are oriented parallel to shorter face of the crystals. In very few cases striations parallel to the longer face are also observed. These studies suggest that the growth occurs by 2D nucleation. Further chemical etching technique has been employed to study dislocations in these crystals. The dislocations are randomly distributed, they are mainly observed at the edges of the crystal. The average dislocation density is about $4 \times 10^5/\mathrm{cm}^2$. Mechanical characterization has been done by Vicker's microhardness technique. The work-hardening index number (n) for these crystals is about 1.9 which is close to theoretically expected value of 2. The hardness studies made on about 50 crystals suggest that hardness (H_v) value is about 76 ± 1 kg/mm^2.

Keywords : Surface studies, etching, microhardness.

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1. Introduction

It is well known that some organic crystals are good NLO materials but their applications are limited due to their poor mechanical properties, whereas inorganic NLO materials show good mechanical and thermal properties but posses modest optical nonlinearities. To solve this problem work has been initiated on the growth of semi-organic NLO materials [1–3]. Zinc (tris) thiourea sulphate (ZTS) is one such material belongs to the family of semi-organic nonlinear optical (NLO) materials. These crystals can be grown comfortably from solution at moderate temperatures. They crystallize in the non-centrosymmetric orthorhombic with space group Pca2_1 (point group mm2). The lattice parameters are reported to be a = 11.26 Å, b = 7.73 Å, c = 5.491 Å [4]. ZTS

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crystal has drawn considerable interest as a potential material for second harmonic generation (SHG) where SHG efficiency is 1.2 times that of KDP and it is used as a potential material for the use as electro-optic modulator also [3]. Venkataramanan and co-workers [5] studied the effect of laser damage in ZTS at a wavelength of 1064 nm and 532 nm using Nd : YAG laser, they observed that ZTS has laser damage threshold of the order of Gw/cm^2 which is comparable to NLO crystals such as KTP and BBO. Due to its importance, it has attracted many people but most of the work has been confined to its growth, spectral and thermal analysis studies only [1]. Systematic study is lacking on surface studies, dislocations and hardness of these crystals. These studies are important because they (surface studies) help in understanding the possible growth mechanism of these crystals, dislocations and hardness studies help in understanding the strength of the crystals. In view of this we have undertaken growth of ZTS crystals, particularly attention has been focused on the systematic study of as-grown faces of these crystals, dislocations and microhardness.

2. Experimental

Zinc (tris) sulphate (ZTS) was synthesized at 30°C by dissolving 3 : 1 ratio of thiourea and zinc sulphate in water [1].

$$ZnSO_4 + 3CS(NH_2)_2 \rightarrow Zn[CS(NH_2)_2]3SO_4$$

The solution was thoroughly stirred using a magnetic stirrer and white crystalline ZTS was formed, the synthesized substance was purified by repeated recrystallization process. The saturated solution of ZTS was prepared using deionized double distilled water at 30°C. The solution was continuously stirred at least for one hour to ensure concentration over the entire volume of the solution. Now the solution is transferred to a constant temperature bath of accuracy ±0.1°C. Initially the temperature of the solution was raised to 35°C and slowly brought back to 30°C in a period of 3 to 4 hours. Now the solution was allowed for very slow evaporation. Crystals of good quality of size 1 cm along one edge were obtained in a period of three weeks. Chemical etching technique was employed to study dislocations in these crystals. Microhardness measurements were made using Leitz-Wetzlar hardness tester fitted with a Vicker's diamond indenter. Hardness values (H_v) are calculated from the expression

$$H_v = 1.854 \ P/d^2 \ \text{kg/mm}^2$$

where P is the load applied in g and d the diagonal length in μ. Each value is atleast the average of four close measurements.

3. Results and discussion

3.1. Crystal growth and surface studies :

Figure 1(a) shows the crystals of ZTS grown from its aqueous solution. These crystals are essentially bounded by {100}, {010}, {001} and {012} faces as shown by line diagram (Figure 1(b)). In all these crystals {100} and {010} faces grew larger than other faces. The observed morphology of these crystals is similar to that reported earlier [1,3].

Figure 1(a). As-grown crystals of ZTS ($m \times 1.2$).
*m–magnification

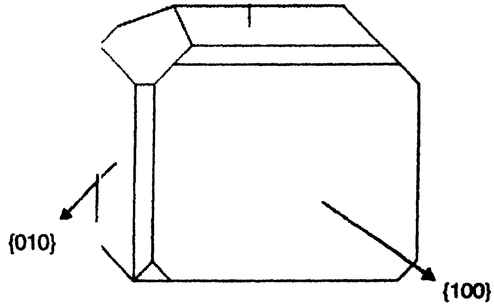
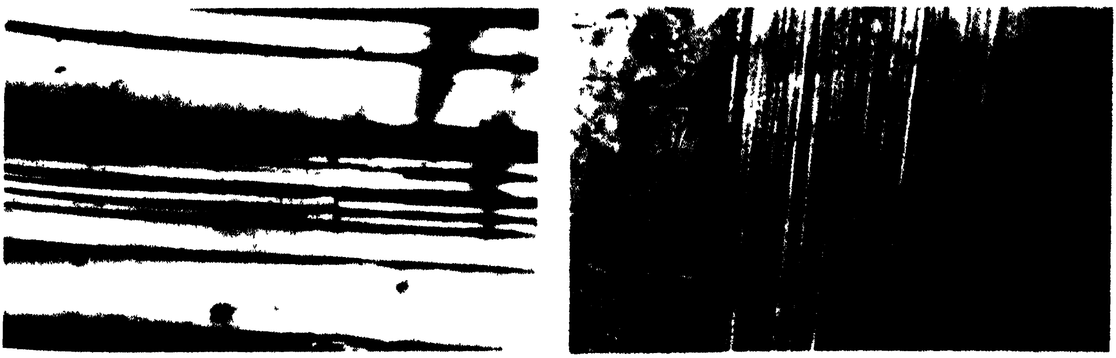


Figure 1(b). Line diagram of ZTS crystal.

It is well known that when the as-grown crystals, particularly from solution grown observed under a good reflection microscope reveal some typical growth features. They include growth spirals, hillocks, overgrowths, striations *etc.* These are not only interesting to see but help in understanding the growth mechanism of the crystals. In view of this an attempt has been made to understand the growth process of these crystals, for which at least 30 as-grown crystals are studied under reflection microscope. {100} faces grow to a considerable size, hence, the studies are confined to these faces only. Most of these faces reveal typical striations (Figure 2(a)), which are parallel to the shorter edge of the crystal. It is important to mention that the striations do not propagate continuously from one end to other. Mostly they appear at the edges and progress towards the center but after propagating to some extent they become diffusing. In few cases the striations appeared parallel to longer faces also (Figure 2(b)).



(a) (b)

Figure 2. Typical striations on as-grown {100} face of ZTS crystals ($m \times 100$).
(a) Parallel to shorter face ($m \times 100$) and (b) Parallel to longer face ($m \times 100$).
*m–magnification

Sangwal [6] pointed out that the cause of the striations could be due to fluctuations in growth conditions such as sudden changes in temperature, cooling rate, convection of the solution or melt and concluded that these features are mostly due two dimensional growth mechanism. Prasad [7] also attributed different types of striations observed on FeS_2 crystals to two dimensional (2D) growth nucleation. In the present studies we have not observed any growth spirals except striations. These studies suggest that these crystals appear to grow by 2D growth process, particularly by layer growth mechanism. Further the observation of striations at the edges suggests that the growth process initiates at the edges and spreads towards the center.

Figure 3(a) shows a thin overgrowth on {100} face of ZTS crystals, it is interesting to note that some typical interlaced pattern are observed on this flake. Van Enckevort and Jetten [8] observed some typical growth steps on {010} face of KAP crystals. From their sophisticated microscopic studies pointed out that they originate from two growth centers, which were observed to be screw dislocation sources. Prasad [9] observed interlaced step pattern on *n*-pentadecanoic acid crystals, attributed the spreading of these steps to as due to screw dislocations or 2D growth mechanism. In the present work the crystals are grown by slow evaporation method. Therefore the supersaturation normally is higher than the spiral growth range, hence it is felt that screw dislocation mechanism may not be responsible for the formation of steps. The reason for the formation of interlacing steps appears to be due to nucleation and propagation of steps (Figure 3(b)) from two 2D sources (S_1, S_2) once they interact with each other form interlacing patterns. Figure 3c shows etch pattern on and around the overgrowth the distribution of etch pits is random.

3.2. Chemical etching :

Chemical etching technique has been employed to study dislocations in these crystals. In view of the meager information on etching studies on these crystals [10,5], a number of etchants were tried (Table 1). Good etching action was observed by the mixture of 1 part of acetic acid + 2 parts of formic acid the etching time is about 20 sec. Figure 4(a) shows etch pattern observed with this etchant on {100} faces of ZTS crystal, the etch pits are more or less rectangular in shape, the longer sides of the etch pits are parallel to shorter face of the crystals. Figure (4b and 4c) shows the successive etch pattern photographs on ZTS, the etching timings are 20 sec and 30 sec. It can be seen from these photographs that all the etch pits of Figure 4(b) persist in 4(c) with increase in size indicating that etch pits are formed at the sites of dislocations only. The distribution of pits is not uniform, it is more at the edges than at other regions. The average density of dislocations is about $4 \times 10^5/cm^2$.

3.3. Microhardness studies :

Hardness is an important solid state property depends on different parameters such as

Figure 3(a). Typical thin overgrowth and interlacing steps on {100} face of ZTS crystal ($m \times 100$).
*m–magnification

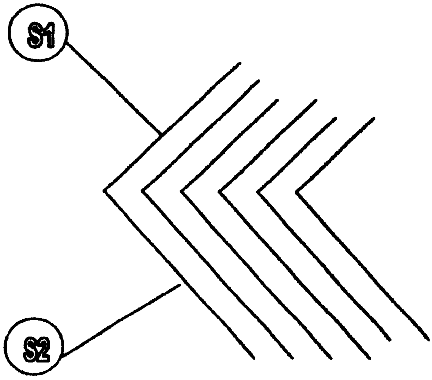


Figure 3(b). Line diagram of interlacing steps.

Figure 3(c). Etch pit pattern observed on and around of overgrowth of ZTS Crystal ($m \times 100$).
*m–magnification

Table 1. Action of various etchants on crystal surface of ZTS.

Etchant	Crystal face	Action
(1) Methanol	{100}	No etching action
(2) Ethanol	{100}	No etching action
(3) Water	{100}	Polishing action
(4) Acetic acid	{100}	No etching action
(5) Formic acid	{100}	No etching action
(6) Acetic + Formic acid (1 : 2)	{100}	Well-defined etch pits
(7) Acetic + Formic acid (1 : 3)	{100}	Etching action increases
(8) Acetic + Formic acid (1 : 4)	{100}	Etching action increases and surface becomes rough

interatomic spacing, lattice energy, Debye temperature, elastic constants *etc.* The microhardness technique is a rapid and nondestructive method to study deformation of crystals. The variation of H_v with load ranging from 10 g to 120 g is illustrated in Figure 6. It is evident from this Figure that the H_v value increases initially up to a load

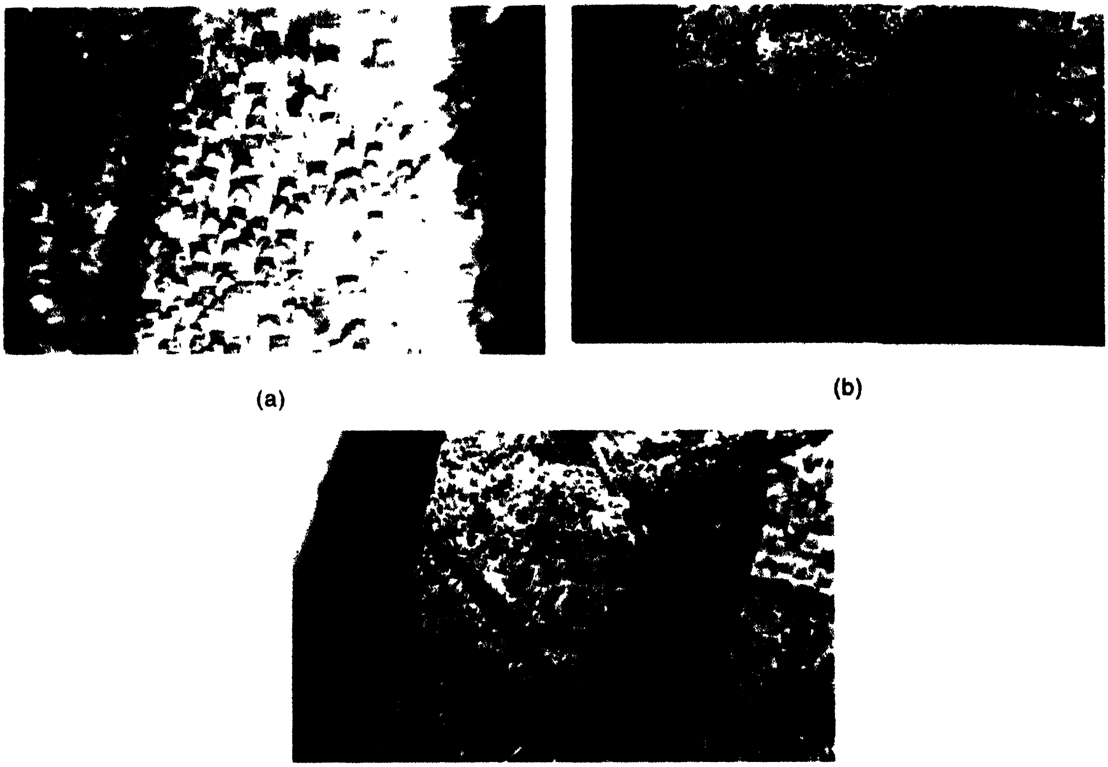


Figure 4. Etch pit pattern observed on {100} face of ZTS crystal.
(a) Etched with acetic + formic acid (1 : 2) (e.t 20 sec) ($m \times 100$),
(b) Successive etch pattern after 20 sec ($m \times 100$) and
(c) Successive etch pattern after 30 sec ($m \times 100$).
*m–magnification

of 60 g and later it becomes load independent. Similar increase in H_v with load was observed on these crystals [1], but this work was limited to 50 g only. In general, load dependence of hardness is expected to be more at lower loads and decreases as the load increases, finally it becomes load independent. This statement appears to be true for simple materials like metals, ionic solids *etc.* where they are mostly mono, di atomic systems [11,12] and in these samples the size of indenter impression increases uniformly with load and produces clear impressions also. The reason for this has been attributed to (i) as the indenter lands on crystal surface under a particular load, the material around it is displaced smoothly [13] and (ii) it could be due to the active participation of slip systems which help in easy glide of the material. In ZTS crystals the atomic arrangement is complex therefore the gliding may not be simple, hence it appears that some kind of reorientation of some of these molecules may take place during indentation process. This could be a reason for showing initial decreases in size

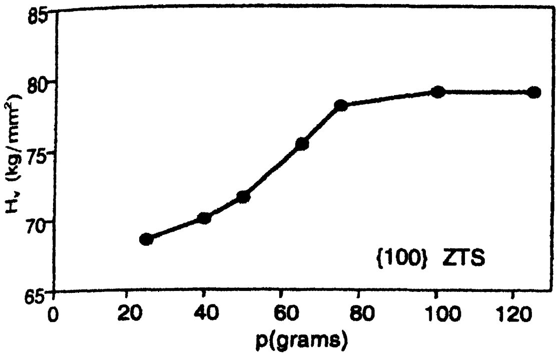


Figure 5. Load variation of hardness for {100} face of ZTS crystal.

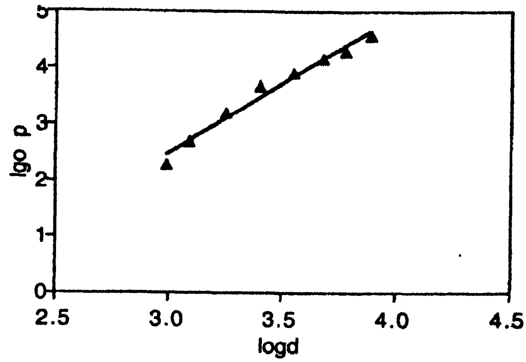


Figure 6. Plots of log P against log d for ZTS crystal.

of impression, which causes an increase in hardness with increasing load. As the load reaches an optimum value about 60 g, some kind of proper alignment appears to take place inside the material thus leading to load independent value above this load. The present load independent hardness value is 78 kg/mm^2, which is close to the value of 82 kg/mm^2 [14].

3.4. *log P against log d plots :*

The load variation can be interpreted by using Meyer's law $P = ad^n$, where 'P' is the load applied, 'd' is the diagonal length of impression, 'a' and 'n' are constants. Figure 7 shows the variation of log P against log d for these crystals. From the slope the value of 'n' has been estimated, it turns out to be 1.9 which is close to 2 as

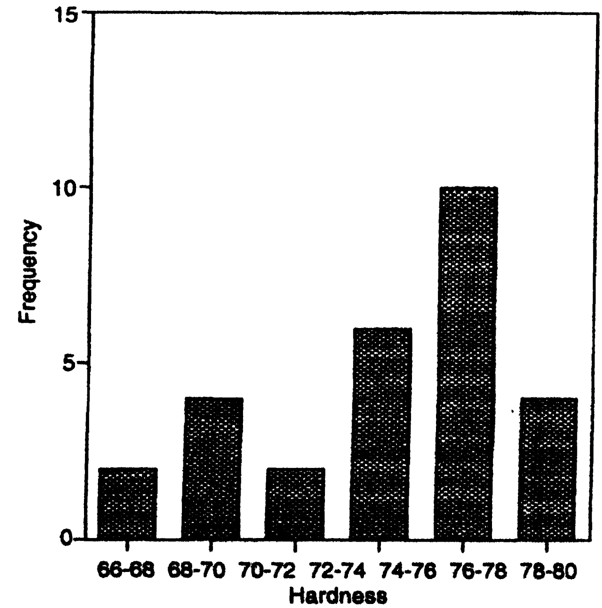


Figure 7. Histogram showing variation of hardness for ZTS crystal.

theoretically expected, this is called as Meyer's index number or work-hardening index also. It has been observed in this laboratory that unlike melt grown crystals, solution grown crystals such as alums, $NaClO_3$, $NaBrO_3$, alkaline earth nitrates, ADP and KDP *etc.* have shown considerable variation in hardness value, even in the crystals grown in the same crop [15–17]. In order to understand this indentation studies have been carried out atleast on about 50 ZTS crystals in the load independent region [P = 75 g], the hardness data is shown by histogram (Figure 8). It can be noticed from this diagram that maximum hardness value varies from 76 kg/mm^2 to 78 kg/mm^2 suggesting that this is the most possible value for these crystals.

4. Conclusions

(i) Typical oriented striations are observed on {100} faces of ZTS crystals suggesting that the growth appears to be due to 2D mechanism.

(ii) 1 : 2 parts of acetic and formic acids mixture acts as good etching agent to reveal dislocations in these crystals.

(iii) The microhardness study shows typical increase in hardness and reaches a load independent value of 76 ± 1 kg/mm^2.

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